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14. ABSTRACT A novel UV-assisted MOMBE system has been developed enabling intense UV irradiation of films during growth. High quality, heavily (unintentionally) carbon-doped GaN is successfully grown by NH <sub>3</sub> -based MOMBE and for the first time InGa <sub>0.5</sub> N, AlGa <sub>0.5</sub> N, and magnesium-doped GaN are demonstrated by NH <sub>3</sub> -based MOMBE. Intense UV irradiation of films during NH <sub>3</sub> -based MOMBE significantly enhances photo-desorption of species during the growth process, subsequently affecting the resultant InGa <sub>0.5</sub> N alloy composition, carbon dopant concentration, or magnesium dopant concentration. A digital micromirror device is introduced to pattern incident UV radiation during InGa <sub>0.5</sub> N growth, demonstrating that the effects of photoexcitation during MOMBE which have been proposed, discovered, and identified by this work indeed can be leveraged to deposit an InGa <sub>0.5</sub> N film that is compositionally patterned within the growth plane. The results demonstrate that the new approach presented herein is possible for the 3D Epitaxy (3DE) of III-Nitrides if additional challenges in practical implementation can be overcome.					
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**LABORATORY INSTRUMENTATION DESIGN RESEARCH FOR SCALEABLE  
NEXT GENERATION EPITAXY:  
NON-EQUILIBRIUM WIDE APPLICATION EPITAXIAL PATTERNING BY  
INTELLIGENT CONTROL (NEW-EPIC)**

**VOLUME I**

**3D COMPOSITION/DOPING CONTROL VIA MICROMIRROR PATTERNED DEEP  
UV PHOTODESORPTION**

**REVOLUTIONARY IN SITU CHARACTERIZATION/CONTROL**

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**20090807017**

## SUMMARY

A novel UV-assisted MOMBE system has been developed enabling intense UV irradiation of films during growth. High quality, heavily (unintentionally) carbon-doped GaN is successfully grown by  $\text{NH}_3$ -based MOMBE and for the first time InGaN, AlGaIn, and magnesium-doped GaN are demonstrated by  $\text{NH}_3$ -based MOMBE. Intense UV irradiation of films during  $\text{NH}_3$ -based MOMBE significantly enhances photo-desorption of species during the growth process, subsequently affecting the resultant InGaIn alloy composition, carbon dopant concentration, or magnesium dopant concentration. A digital micromirror device is introduced to pattern incident UV radiation during InGaIn growth, demonstrating that the effects of photoexcitation during MOMBE which have been proposed, discovered, and identified by this work indeed can be leveraged to deposit an InGaIn film that is compositionally patterned within the growth plane. The results demonstrate that the new approach presented herein is possible for the 3D Epitaxy (3DE) of III-Nitrides if additional challenges in practical implementation can be overcome.

Increased control over the growth of Mg-doped GaN by plasma-assisted molecular beam epitaxy was achieved by addressing several issues. A new Mg dopant source was implemented, characterized and modeled for p-type doping of GaN. The device enhanced the sticking coefficient of Mg by energizing the outgoing Mg flux, and also allowed the first reported demonstration of an abrupt junction between two non-zero Mg concentrations and a graded Mg-doped GaN film. The significant compensation of Mg acceptors at high dopant concentrations was used advantageously to develop a new ex situ resistivity analysis technique using the energy distributions of SIMS to characterize doping of buried layers. The new technique was used to identify the barrier between conductive and resistive Mg doping for increased Mg concentration, which was then used to optimize Mg-doped GaN. Because Mg doping exhibits a dependence upon the growth regime, a new growth and regime characterization technique was developed using specific RHEED intensity responses to repeat growth conditions. During the development of this technique, a new surface kinetics growth model for III-nitrides was discovered based on DMS observations, which suggests preferential buildup of the metal bilayer before growth begins with an unfamiliar cation-anion exchange process initially upon metal shutter opening. Using the new RHEED growth and regime characterization technique, a new growth technique called metal modulated epitaxy (MME) was developed to increase repeatability, uniformity and smoothness. The MME technique was enhanced with a closed-loop control using real-time feedback from RHEED transients to control shutter transitions. This enhancement, called "smart shuttering," led to improved growth rate and further improvement of surface roughness and grain size, which were repeatable within low percentages. Effects of smart-shuttering MME were observed with Si, Mg and In during GaN growths. Repeatable Mg-doped GaN was achieved with a variation of less than 8%, and a peak hole carrier concentration of  $4.7 \times 10^{18} \text{ cm}^{-3}$ .



### **Students supported under this MURI:**

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David Pritchett  
Shawn Burnham

#### *Undergraduate (1)*

Brian Smith

### **Detailed Technical Discussion:**

Detailed technical discussion can be found in the papers listed in the next section and in the following included works:

D. Pritchett, "Novel III-Nitride Growth by Ultraviolet Radiation Assisted Metal Organic Molecular Beam Epitaxy," *Ph. D. Thesis, Georgia Institute of Technology*, 2009

D. Billingsley, W. Henderson, D. Pritchett, and W. Alan Doolittle, "Growth and Characterization of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  via Ammonia-based Metal Organic Molecular Beam Epitaxy," *Journal of Crystal Growth* accepted 2008.

S. D. Burnham, "Improved Understanding and Control of Magnesium-Doped Gallium Nitride by Plasma Assisted Molecular Beam Epitaxy," *Ph. D. Thesis, Georgia Institute of Technology*, 2007

### **Publications:**

D. Billingsley, W. Henderson, D. Pritchett, W. A. Doolittle, "Optimization of GaN Surface Morphology Grown by Ammonia-Based Metal Organic Molecular Beam Epitaxy," *in preparation*.

D. Billingsley, W. Henderson, D. Pritchett, and W. A. Doolittle, "Improved Understanding of the Growth of AlGa<sub>N</sub> Grown by Ammonia-Based Metal Organic Molecular Beam Epitaxy," *in preparation*.

D. Pritchett, W. Henderson, D. Billingsley, W. Alan Doolittle, "Mg doped GaN and Intentional Mg Dopant Modulation *in situ* by  $\text{NH}_3$ -based Metal Organic Molecular Beam Epitaxy," *in preparation*.

D. Pritchett, D. Billingsley, W. Henderson, W. A. Doolittle, "Growth Regimes of GaN during  $\text{NH}_3$ -based Metal Organic Molecular Beam Epitaxy," *in preparation*.

D. Billingsley, W. Henderson, D. Pritchett, and W. Alan Doolittle, "Growth and Characterization of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  via Ammonia-based Metal Organic Molecular Beam Epitaxy," *Journal of Crystal Growth* accepted 2008.

D. Pritchett, W. Henderson, D. Billingsley, and W. A. Doolittle, "Mixed Alkyl Exchange and Exploitable Surface Interactions in InGaN by  $\text{NH}_3$ -based Metal Organic Molecular Beam Epitaxy," *Journal of Crystal Growth* 310, 5297 (2008).

S. D. Burnham, G. Namkoong, D. C. Look, B. Clafin, and W. A. Doolittle, "Reproducible Increased Mg Incorporation and Large Hole Concentration in GaN using Metal Modulated Epitaxy," *Journal of Applied Physics* 104, 024902 (2008).

D. Billingsley, D. Pritchett, W. Henderson, A. G. Carver, S. D. Burnham, and W. A. Doolittle, "Investigation into the use of Molecular Hydrogen on the Growth of Gallium Nitride via Metal-organic Molecular Beam Epitaxy," *Physica Status Solidi C* 5, 1723 (2008).

D. Pritchett, W. Henderson, D. Billingsley, and W. A. Doolittle, "InGaN Compositional Patterning by Ultraviolet Photoexcitation during  $\text{NH}_3$ -based MOMBE - A Pathway to 3D Epitaxy," *Physica Status Solidi C* 5, 1726 (2008).

S. D. Burnham, G. Namkoong, K.-K. Lee, and W. A. Doolittle, "Reproducible Reflection High Energy Electron Diffraction Signatures for Improvement of AlN using in situ Growth Regime Characterization," *Journal of Vacuum Science and Technology B*, 25, 1009 (2007).

Q. Sun, A. Selloni, T. H. Myers, and W. A. Doolittle, "Oxygen adsorption and incorporation at irradiated GaN(0001) and GaN(000-1) surfaces: first-principles density-functional calculations," *Physical Review B*, 74, 195317 (2006)

S. D. Burnham, E. W. Thomas, and W. A. Doolittle, "Resistivity Analysis of Epitaxially Grown, Doped Semiconductors using Energy Dependent Secondary Ion Mass Spectroscopy," *Journal of Applied Physics*, 100, 113719 (2006).

S. D. Burnham and W. A. Doolittle, "In situ Growth Regime Characterization of AlN using Reflection High Energy Electron Diffraction," *Journal of Vacuum Science & Technology B*, 24, 2100 (2006).

Q. Sun, A. Selloni, T. H. Myers, and W. A. Doolittle, "Energetics of Mg incorporation at GaN(0001) and GaN(000-1) surfaces," *Physical Review B*, 73 155337, (2006)

D. Pritchett, W. Henderson, S. D. Burnham, and W. A. Doolittle, "Influence of Growth Conditions and Surface Reaction Byproducts on GaN Grown via Metal Organic Molecular Beam Epitaxy: Toward an Understanding of Surface Reaction Chemistry," *Journal of Electronic Materials* 35, 562 (2006).

S. D. Burnham, G. Namkoong, W. Henderson, and W. A. Doolittle, "Mg doped GaN using a Valved, Thermally Energetic Source: Enhanced Incorporation, and Control," *Journal of Crystal Growth*, 279, 26 (2005).

#### **Patents:**

W. A. Doolittle, D. Pritchett, and W. Henderson, "Maskless and Dynamic AlInGaN Compositional and Doping Patterning for Three Dimensional Epitaxy," *U.S. Patent Pending*, February 19, 2007.

#### **Presentations:**

D. Pritchett, D. Billingsley, W. Henderson, and W. A. Doolittle, "Toward Engineered 3-Dimensional Epitaxy using Micro-mirror Patterned Photo-assisted Epitaxy," *2008 Electronic Materials Conference*, June 27, 2008

D. Pritchett, W. Henderson, D. Billingsley, and W. A. Doolittle, "InGaN Compositional Control by Ultraviolet Photoexcitation during NH<sub>3</sub>-based MOMBE - A Pathway to 3D Epitaxy," *7th International Conference of Nitride Semiconductors*, September 18, 2007.

D. Billingsley, D. Pritchett, S. D. Burnham, W. Henderson, and W. A. Doolittle, "Investigation into the Use of Molecular Hydrogen on the Growth of Gallium Nitride via Metal-Organic Molecular Beam Epitaxy," *7th International Conference of Nitride Semiconductors*, September 18, 2007.

S. D. Burnham and W. A. Doolittle, "A New Growth Kinetics Model for AlN, Based on DMS Observations," *2007 Workshop on Compound Semiconductor Materials and Devices*, May 20, 2007.

D. Pritchett, D. Billingsley, W. Henderson, and W. A. Doolittle, "Influence of Ultraviolet Photoexcitation on the Growth of InGaN via NH<sub>3</sub>-based MOMBE," *2007 Workshop on Compound Semiconductor Materials and Devices*, February 19, 2007.

D. Billingsley, D. Pritchett, W. Henderson, E. Trybus, K.K. Lee, and W. A. Doolittle, "Influence of Surface Nitridation on Gallium Nitride Grown via Ammonia based Metal Organic Molecular Beam Epitaxy," *2006 North American Molecular Beam Epitaxy Conference*, October 9, 2006.

S. D. Burnham, G. Namkoong, K.-K. Lee, and W. A. Doolittle, "Reproducible RHEED Signatures for *in situ* Growth Regime Characterization of AlN," *24th North American Conference on Molecular Beam Epitaxy*, October 8, 2006.

D. Pritchett, W. Henderson, S. D. Burnham, and W. A. Doolittle, "Influence of Intense Ultraviolet Photoexcitation on Surface Reactions during Gallium Nitride Growth via Metal Organic Molecular Beam Epitaxy," *33rd Physics and Chemistry of Semiconductor Interfaces Conference*, January 17, 2006.

S. D. Burnham and W. A. Doolittle, "Quantitative, *In Situ* Growth Regime Characterization of AlN Using Reflection High Energy Electron Diffraction," *33rd Conference on the Physics and Chemistry of Semiconductor Interfaces*, January 15, 2006.

D. Pritchett, S. D. Burnham, W. Henderson, and W. A. Doolittle, "Metalorganic Molecular Beam Epitaxy (MOMBE) of GaN: Towards an Understanding of Surface Reaction Chemistry," *2005 Electronic Materials Conference*, June 23, 2005.

S. D. Burnham, G. Namkoong, and W. A. Doolittle, "New Physical Understanding of the Nature of Sublimed Mg and Mg Doped GaN," *Workshop on Compound Semiconductor Materials and Devices*, February 22, 2005.

S. D. Burnham, W. A. Doolittle, G. Namkoong, and W. Henderson, "Mg doped GaN using a Valved, Thermally Energetic Source: Enhanced Incorporation, Control and Quantitative Optimization," *Material Research Society Symposium Proceedings*, November 29, 2004.

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**NOVEL III-NITRIDE GROWTH BY ULTRAVIOLET RADIATION  
ASSISTED METAL ORGANIC MOLECULAR BEAM EPITAXY**

A Dissertation  
Presented to  
The Academic Faculty

By

David C. Pritchett

In Partial Fulfillment  
Of the Requirements for the Degree  
Doctor of Philosophy in Electrical and Computer Engineering

Georgia Institute of Technology

January 2009

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**NOVEL III-NITRIDE GROWTH BY ULTRAVIOLET RADIATION  
ASSISTED METAL ORGANIC MOLECULAR BEAM EPITAXY**

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ILC (presently Datapath)

**NEW-EPIC MURI  
ANNUAL REPORT September 2007  
ICN Number: F49620-03-1-0330**

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Georgia Institute of Technology

**Section 1) Georgia Tech Contribution - UV MOMBE Epitaxial Patterning**

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**2007 Paper/Patent/Presentation Contributions**

W. A. Doolittle, D. Pritchett, W. Henderson, "Maskless and Dynamic AlInGaN Compositional and Doping Patterning for Three Dimensional Epitaxy," U. S. Patent Pending, February 19, 2007.

D. Pritchett, D. Billingsley, W. Henderson, and W. A. Doolittle, "Influence of Ultraviolet Photoexcitation on the Growth of InGaN via NH<sub>3</sub>-based MOMBE," *2007 Workshop on Compound Semiconductor Materials and Devices*, February 19, 2007.

D. Pritchett, W. Henderson, D. Billingsley, W. A. Doolittle, "InGaN Compositional Control by Ultraviolet Photoexcitation during NH<sub>3</sub>-based MOMBE - A Pathway to 3D Epitaxy," *7th International Conference of Nitride Semiconductors*, September 18, 2007.

D. Billingsley, D. Pritchett, S. D. Burnham, W. Henderson, W. A. Doolittle, "Investigation into the Use of Molecular Hydrogen on the Growth of Gallium Nitride via Metal-Organic Molecular Beam Epitaxy," *7th International Conference of Nitride Semiconductors*, September 18, 2007.

D. Pritchett, W. Henderson, D. Billingsley, W. A. Doolittle, "Mixed alkyl exchange and exploitable surface interactions in InGaN by NH<sub>3</sub>-based metal organic molecular beam epitaxy," *Journal of Crystal Growth*, submitted November 20, 2007

D. Pritchett, W. Henderson, D. Billingsley, W. A. Doolittle, "InGaN Compositional Patterning by Ultraviolet Photoexcitation during NH<sub>3</sub>-based MOMBE - A Pathway to 3D Epitaxy," *Physica Status Solidi*, accepted December 16, 2007.



D. Billingsley, D. Pritchett, W. Henderson, A. G. Carver, S. D. Burnham, W. A. Doolittle,  
"Investigation into the use of molecular hydrogen on the growth of gallium nitride via metal-  
organic molecular beam epitaxy," *Physica Status Solidi*, accepted December 16, 2007.

## Summary

Over the past year under the NEW-EPIC MURI group at Georgia Tech has made the following advances:

- Increased understanding of InGaN growth characteristics by  $\text{NH}_3$ -based MOMBE, producing consistent InGaN films (peak 19% In, repeatable 10% In).
- This deeper understanding has enabled successful compositional patterning of InGaN using *in situ* digital micromirror device (DMD) patterning of ultraviolet (UV) photoexcitation.
- Increased understanding of the role of  $\text{H}_2$  during GaN growth.

In addition, the following has also been investigated to further enhance and understand III-N growth by  $\text{NH}_3$ -based MOMBE:

- The growth of AlN alloys by  $\text{NH}_3$ -based MOMBE.
- The novel use  $\text{SiBr}_4$  for Si doping of III-Nitrides.

## InGaN by NH<sub>3</sub>-based MOMBE

InGaN films with up to 19% indium composition have been demonstrated for the first time by NH<sub>3</sub>-based MOMBE. Significant variations in alloy composition, growth rate, and III-alkyl desorption with substrate temperature, V/III and Ga/In have been reported (Fig. 1, Fig. 2). N-limited growth from insufficient NH<sub>3</sub> cracking at 400–660 °C is observed as growth rate increases with increasing NH<sub>3</sub> flow. A physisorbed In/In-methyl surface layer has been suspected to further inhibit growth by blocking precursor adsorption in cases of highly deficient active N and high In flux. Desorbing III-alkyl species in the presence of trimethylindium (TMIn) (Fig. 3) have been identified as predominately III-methyl species (Table 1, Table 2) resulting from mixed alkyl (ethyl-gallium with methyl-indium) interactions at the growth interface. The observed variations in III-alkyl desorption with changing growth conditions suggest that methyl groups attach to decomposed triethylgallium (TEGa) species and do not incorporate. Instead, the methyl groups effectively scavenge surface Ga atoms for N-limited, high In/In-methyl surface coverage growth.

The results demonstrate for the first time that NH<sub>3</sub>-based MOMBE is capable of In<sub>x</sub>Ga<sub>1-x</sub>N growth, but active N, indium surface coverage, and mixed alkyl scavenging must be carefully considered. These three interdependent variables set an upper limit to In incorporation but also provide sensitive, exploitable mechanisms enabling novel three dimensional device structures created by intentional and controllable lateral composition inhomogeneity.

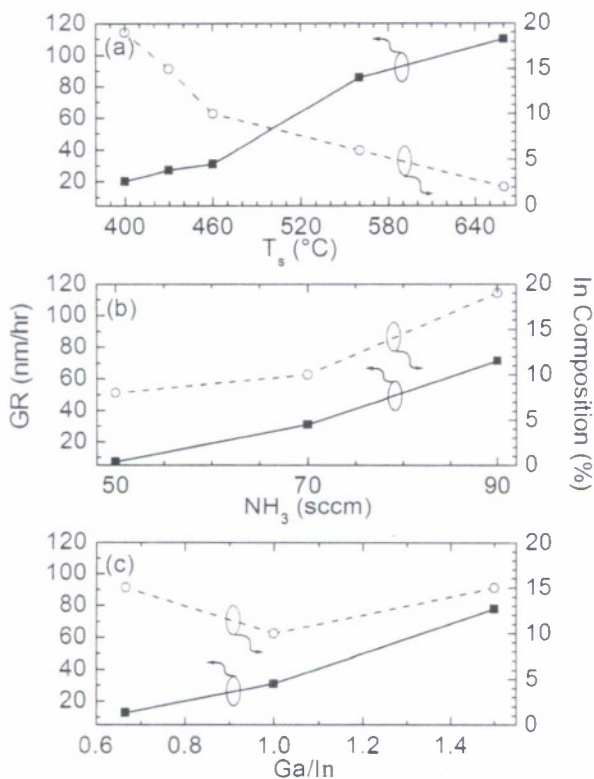


FIG. 1. Growth rate and composition variation for  $\text{In}_x\text{Ga}_{1-x}\text{N}$  grown at (a)  $T_s = 400$ -660 °C, (b)  $\text{NH}_3 = 50$ , 70, and 90 sccm, and (c)  $\text{Ga/In} = 2/3$ , 1, and  $3/2$ . Only the dominant indium composition is shown.

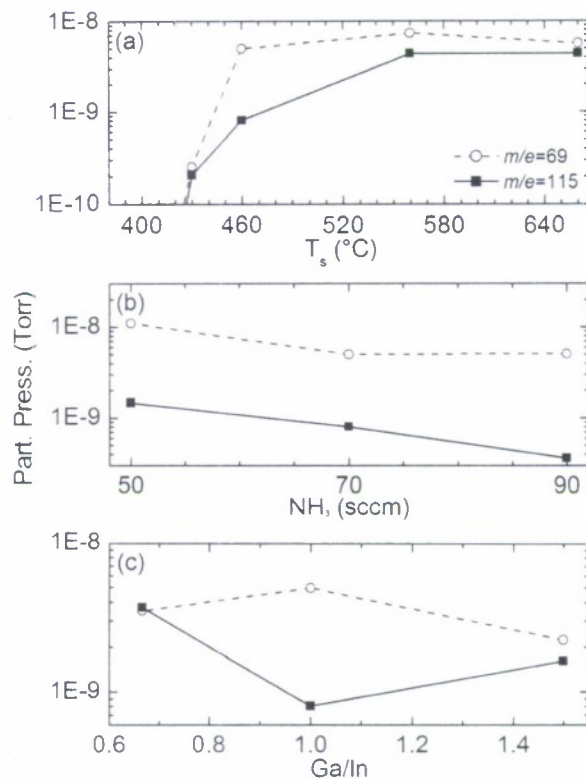


FIG. 2. Partial pressures of  $m/e = 69$  and 115 (with Ga-alkyl contributions removed) during  $\text{In}_x\text{Ga}_{1-x}\text{N}$  growth for (a)  $T_s = 400$ -660 °C, (b)  $\text{NH}_3 = 50$ , 70, and 90 sccm, and (c)  $\text{Ga/In} = 2/3$ , 1, and  $3/2$ . Signals  $m/e = 69$  and 115 have been shown to accurately represent the desorption of Ga- and In-  $(\text{CH}_3)_x$  species respectively.

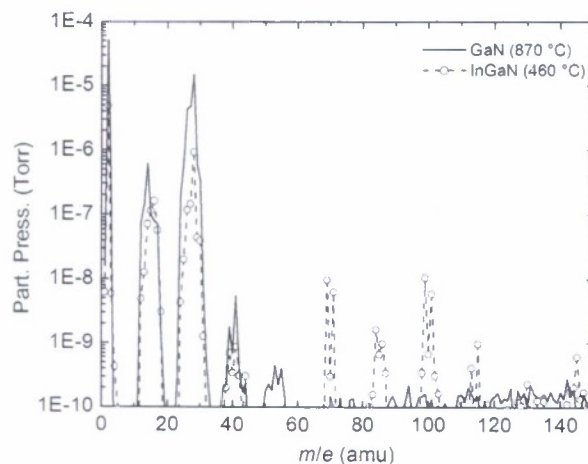


FIG. 3. RGA mass spectra of representative GaN and InGaN growths in the present reactor.



TABLE 1. Calculated mass spectrum of desorbing Ga-alkyls during present  $\text{In}_x\text{Ga}_{1-x}\text{N}$  growths.

$m/e$ (amu)	Ga Species, Abundance (%)	Name
69	$26.81 \pm 1.19$	Ga
71	$16.86 \pm 0.88$	
84	$04.46 \pm 0.11$	MMGa, $\text{GaCH}_3$
86	$02.89 \pm 0.17$	
99	$29.60 \pm 0.71$	DMGa, $\text{Ga}(\text{CH}_3)_2$
101	$16.64 \pm 0.84$	
113	$00.71 \pm 0.22$	MMEGa, $\text{Ga}(\text{CH}_3)(\text{C}_2\text{H}_5)$
115	$00.47 \pm 0.15$	
128	$00.57 \pm 0.30$	DMEGa, $\text{Ga}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$
130	$00.38 \pm 0.20$	
143	$00.36 \pm 0.16$	?
145	$00.24 \pm 0.11$	

TABLE 2. Calculated mass spectrum of desorbing In-methyls during present  $\text{In}_x\text{Ga}_{1-x}\text{N}$  growths.

$m/e$ (amu)	In Species, Abundance (%)	Name
113	$02.39 \pm 0.13$	In
115	$53.24 \pm 2.97$	
128	$00.32 \pm 0.03$	MMIn, $\text{InCH}_3$
130	$07.07 \pm 0.63$	
143	$01.59 \pm 0.13$	DMIn, $\text{In}(\text{CH}_3)_2$
145	$35.39 \pm 2.89$	

## InGaN Compositional Patterning *In Situ*

Lateral compositional patterning of InGaN during  $\text{NH}_3$ -based MOMBE by digital micromirror patterning of UV photoexcitation has been demonstrated. Analysis of the growth reaction byproducts suggest that preferential desorption of In/In-methyl species during InGaN surface exposure to an elliptically focused 5 kW Hg-Xe arc lamp ( $\lambda = 365$  nm) inhibits the incorporation of indium (Fig. 4) while increases growth rate by a factor of 4. Localized photoexcitation results in the preferential In/In-methyl desorption (Fig. 5), resulting in indium mole fractions of 0.10 in unexposed regions to as low as 0 in fully exposed regions (Fig. 6, Fig. 8). The detectability limit of x-ray diffraction (XRD) and the blurred projected features are expected to contribute to the modest detection of patterned submillimeter features in the XRD intensity map. However, significantly improved projection contrast ratio has been achieved with additional optics (Fig. 7).

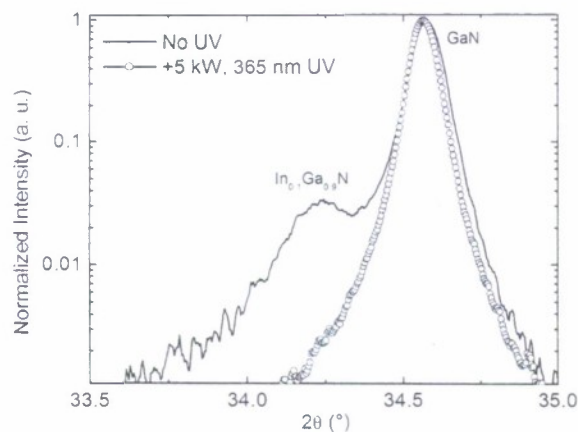


FIG. 4. XRD  $2\theta$ - $\omega$  of  $\text{In}_{0.1}\text{Ga}_{0.9}\text{N}$  (002) with and without *in situ* UV photoexcitation.

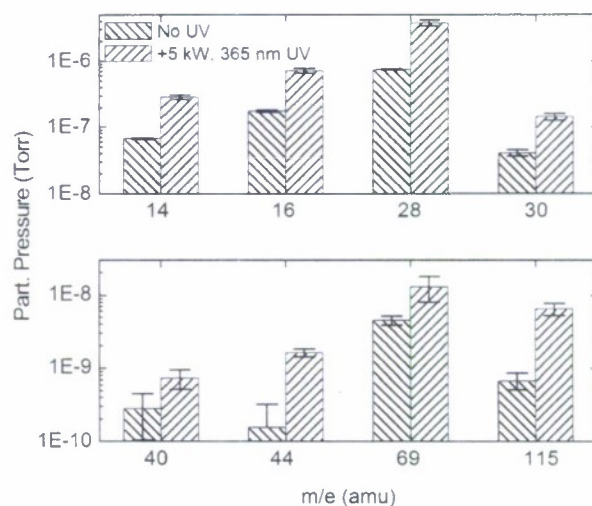


FIG. 5. Partial pressure of signals characteristic of  $\text{NH}_3$  ( $m/e = 14, 16, 28$ ), hydrocarbon byproducts such as ethane ( $m/e = 30$ ), argon ( $m/e = 40$ ),  $\text{CO}_2$  ( $m/e = 44$ ), desorbing Ga-alkyls ( $m/e = 69$ ), and desorbing In-methyls ( $m/e = 115$ ) during InGaN growth with and without *in situ* UV photoexcitation.

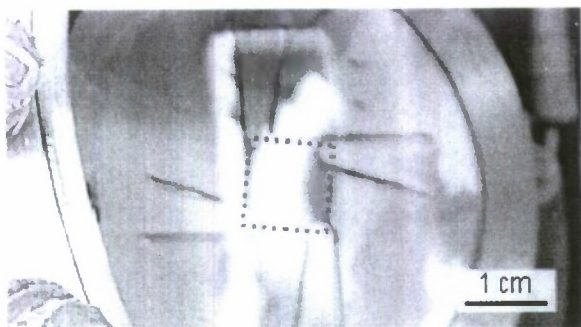


FIG. 6. Visible DMD patterned UV irradiation incident on sample (dotted red box).

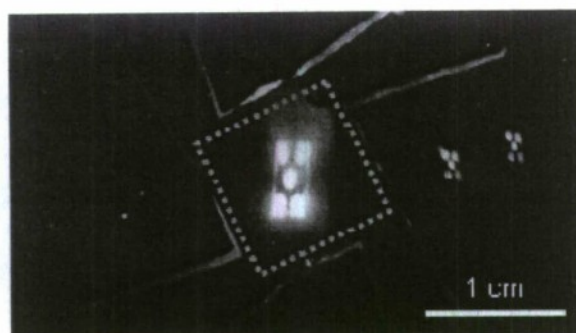


FIG. 7. DMD patterned visible light incident on sample (dotted red box).

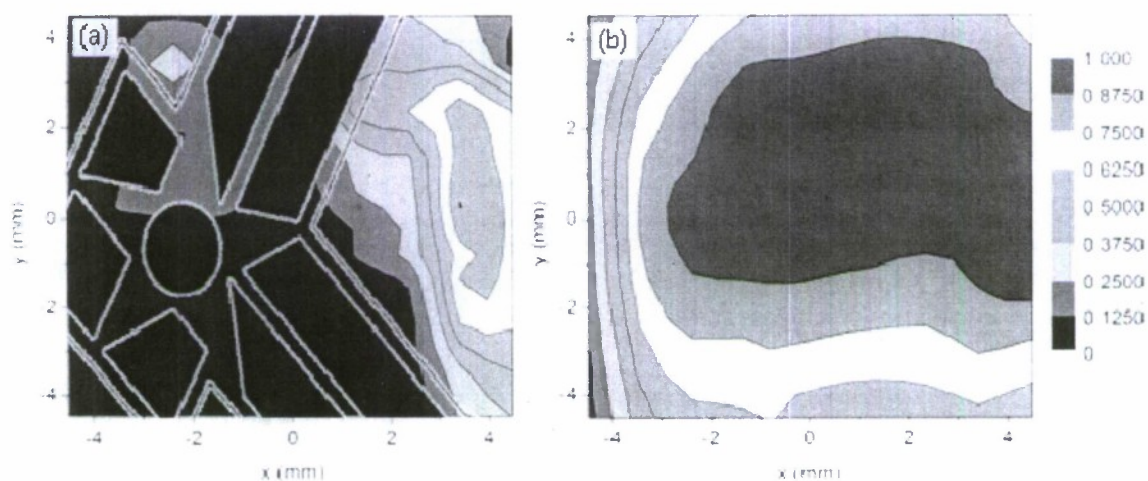


FIG. 8.  $1 \times 1$  mm resolution normalized XRD intensity map of  $\text{In}_{0.1}\text{Ga}_{0.9}\text{N}$  (002) peak of (a) sample exposed to DMD patterned UV irradiation (pattern shown as black overlay) and (b) sample not exposed to UV irradiation.

## GaN:C Variation *In Situ* Using H<sub>2</sub>

Molecular hydrogen (H<sub>2</sub>) has been investigated as a means to vary carbon concentration in NH<sub>3</sub>-based MOMBE. The effects of H<sub>2</sub> on the carbon concentration of GaN was studied using a two-layer GaN structure, with one layer exposed to H<sub>2</sub>. Secondary ion mass spectroscopy (SIMS) shows that H<sub>2</sub> during growth increases the carbon incorporation in GaN by 57% while reducing the growth rate by 18.75% (Fig. 9). These effects of H<sub>2</sub> suggest an increased gallium desorption in the presence of excessive H<sub>2</sub>. Investigation of the effects of atomic hydrogen on the carbon incorporation of III-N during NH<sub>3</sub>-based MOMBE is in progress pending instrumentation enhancements.

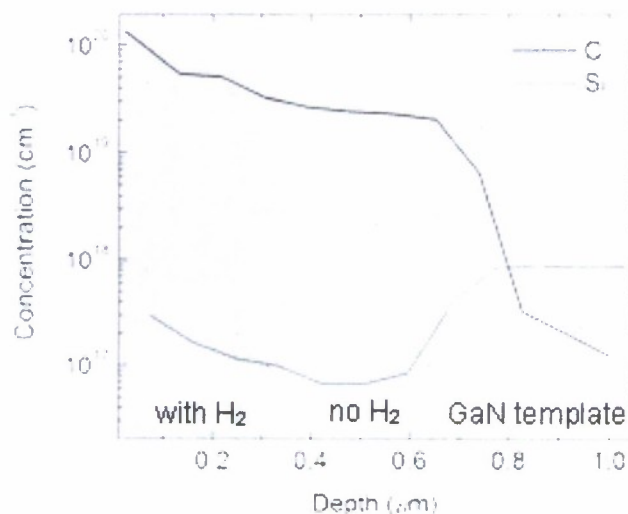


FIG. 9. Carbon concentrations of GaN without H<sub>2</sub> and GaN using H<sub>2</sub> stack structure.



## Improved III-N $\text{NH}_3$ -based Nucleation: AlN and $\text{H}_2$ Substrate Treatment

$\text{NH}_3$ -based MOMBE of GaN and InGaN on sapphire has yielded films of modest crystalline quality compared to advanced MBE and MOCVD techniques. However,  $\text{NH}_3$ -based MOMBE of both GaN and InGaN on commercial GaN templates has demonstrated the high crystalline quality capability of  $\text{NH}_3$ -based MOMBE (Fig. 10). Therefore, sapphire treatment technique and AlN growth are being studied to improve GaN nucleation on sapphire – improving subsequent III-N crystalline quality while providing consistent polarity.

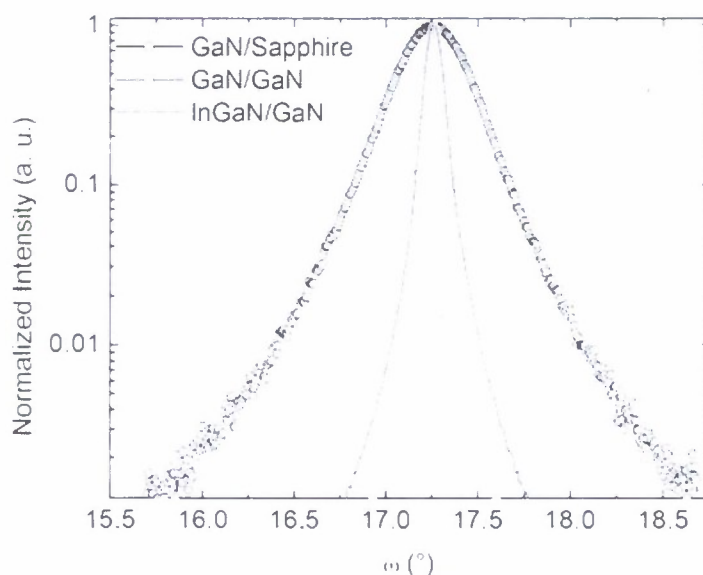


FIG. 10. XRD rocking curve of GaN on sapphire employing  $\text{NH}_3$ -based nucleation layers vs. GaN and InGaN on commercial GaN templates.

The pre-treatment of sapphire with  $\text{H}_2$  prior to ammonia nitridation of sapphire demonstrates a 30% improvement in crystalline quality (inferred from XRD). The pre-treatment is speculated to improve the crystalline quality by enhancing the ammonia nitridation efficiency via chemical reduction of the oxidized sapphire surface, yielding an improved yet incomplete surface conversion to AlN. Also, when the sapphire was pre-treated at 1000 °C for 10 min with  $\text{H}_2$ , a growth rate decrease of ~56% is observed in the subsequent GaN layer (Table 3). Samples  $\text{H}_2$ -treated at 1000 °C for 30 min showed a growth rate decrease of ~28.6%. The decrease in the

growth rate is expected to be the result of polarity inversion caused by the high temperature sapphire pre-treatment.

TABLE 3. Growth rate ( $\mu\text{m/hr}$ ) for GaN films with  $\text{H}_2$  pre-treatment at 500 °C and 1000 °C for 10 and 30 min.

500 °C		1000 °C	
10 min	30 min	10 min	30 min
0.29	0.41	0.207	0.18

The first AlN and AlGa<sub>1-x</sub>N by  $\text{NH}_3$ -based MOMBE using triethylaluminum (TEAl) are being studied. While Al<sub>x</sub>Ga<sub>1-x</sub>N has been demonstrated using dimethylethylamine alane (DMEAA), TEGa was chosen to replace DMEAA due to the high volatility and anticipated mixed-alkyl implications of DMEAA. GaN films grown using only AlN buffers (TEAl precursor, no buffer optimization) exhibit similar crystalline quality (XRD) to the best films grown by  $\text{NH}_3$ -based MOMBE employing low temperature GaN buffers (1000 vs. 800 arcsec XRD rocking curve FWHM 0002). However, challenges in obtaining consistent TEAl delivery are being addressed.

## Si doping of GaN and InGaN

Silicon tetrabromide ( $\text{SiBr}_4$ ) was investigated as a novel Si precursor to overcome challenges with the introduction of disilane for III-N doping in vacuum epitaxy. GaN:Si samples grown using  $\text{SiBr}_4$  demonstrated enhanced band-edge photoluminescence (PL) intensity (Fig. 11). However, a solid phase byproduct results in the growth chamber when using  $\text{SiBr}_4$  (Table 4).

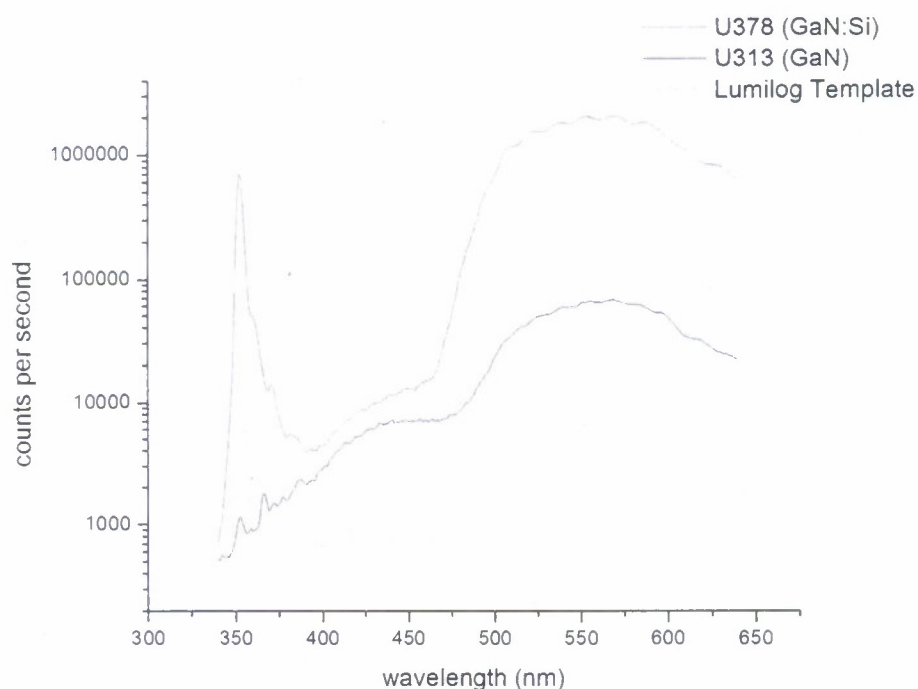


FIG. 11. PL spectra of Si-doped GaN, UID GaN, and GaN template..

TABLE 4. Atomic concentration of residual solid byproduct after introduction of  $\text{SiBr}_4$  (as determined by x-ray photoelectron spectroscopy, XPS).

Br	13.4%
Si	12.4%
C	26.1%
N	9.7%
In	3.0%
O	35.4%

## Future Work

Current and future efforts are focused on the following:

- *Improved understanding of UV-induced  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloy modulation:* UV irradiation during growth has demonstrated significant GaN dopant and  $\text{In}_x\text{Ga}_{1-x}\text{N}$  composition variation. However, the mechanism for reduced indium incorporation in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  films exposed to in situ UV photoexcitation remains unclear. While preferential In/In-methyl desorption has been observed in the presence of UV photoexcitation, both photochemical and thermal explanations are plausible. Therefore, UV photoexcitation effects on  $\text{In}_x\text{Ga}_{1-x}\text{N}$  by  $\text{NH}_3$ -based MOMBE is being studied further, considering additional growth conditions and photoexcitation sources in order to better understand the observed alloy modulation capabilities.
- *$\text{NH}_3$ -based MOMBE of Mg doped GaN and UV-induced dopant modulation:* GaN:Mg by  $\text{NH}_3$ -based MOMBE using  $\text{Cp}_2\text{Mg}$  is currently being investigated and characterized. Moreover, the effects of UV irradiation on Mg doping of GaN by  $\text{NH}_3$ -based MOMBE will be investigated to determine the feasibility of novel, in situ patterning of GaN conductivity type and polarity.
- *Modification and utilization of endemic C doping in  $\text{NH}_3$ -based MOMBE films:* Previous work has demonstrated significant doping level modulation in GaN:C through the use of in situ UV exposure during growth. Future work follows two complementary paths:
  - *Low leakage, high breakdown voltage HEMTs with GaN:C buffer:*  $\text{NH}_3$ -based MOMBE has demonstrated highly resistive GaN by carbon doping greater at  $10^{20} \text{ cm}^{-3}$  concentration. The use of highly resistive GaN:C layers for low leakage HEMT devices will be investigated.
  - *Optimization of GaN in MOMBE environment:* High carbon concentrations associated with the use of metal organic sources are not always useful for device applications; therefore investigations into methods to reduce the carbon levels in the films will be conducted. This improvement in the film quality will widen the possibilities of future devices.
- *Growth of  $\text{Al}_{1-x}\text{Ga}_x\text{N}$  for device applications:*  $\text{Al}_{1-x}\text{Ga}_x\text{N}$  is a material important to the continued development of electronic devices grown in the MOMBE environment. Investigations into the optimization and precise growth of a wide array of  $\text{Al}_{1-x}\text{Ga}_x\text{N}$  compositions will be conducted. Furthermore, the effect of UV irradiation on the deposition of  $\text{Al}_{1-x}\text{Ga}_x\text{N}$  will also be explored.
- *Use of UV-induced alloy modulation for devices:* Alloy composition control through UV irradiation has been demonstrated, and will be extended to the formation of electronic



devices. *In situ* patterning by UV irradiation will greatly reduce the traditional processing steps associated with modern day fabrication.

## Section 2) University of West Virginia Contribution

Dr. Thomas Myers, PI

### Overview

WVU has three separate tasks under this MURI. Under control of surface energetics, we are developing techniques for Modified Surface Energy Epitaxy (MOSEE) by electron-beam excitation. We have demonstrated that e-beam irradiated can be used to modify both growth and dopant incorporation kinetics in GaN, consistent with theoretical predictions developed during this MURI. Under Revolutionary In-Situ Characterization/Control we have demonstrated reflection high energy electron diffraction total angle x-ray fluorescence (RHEED-TRAX) for in-situ surface stoichiometry measurement during growth, and are developing in-situ imaging cathodoluminescence (CL) for measuring temperature and stoichiometry, including inhomogeneities, during growth.

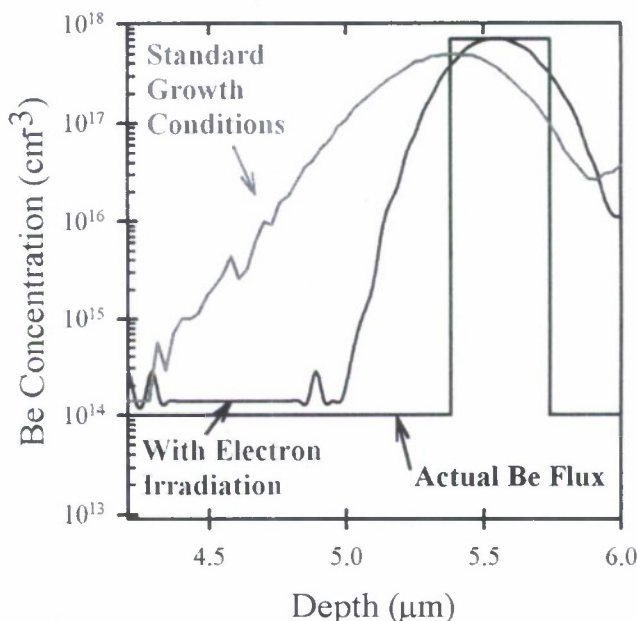


Figure 1 - Effect of electron irradiation on enhancing Be incorporation in Ga-polar GaN during growth

### Technical progress to date

#### Modified Surface Energy Epitaxy (MOSEE) by E-beam excitation

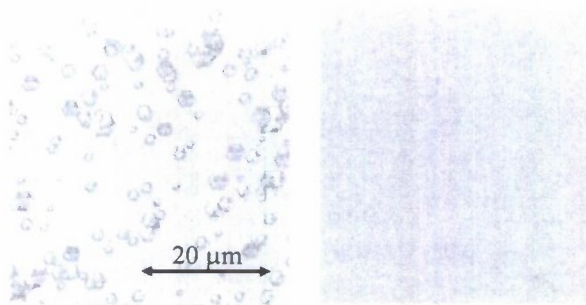


Figure 2 – Demonstration of suppression of inversion domain formation during heavy Be doping of GaN due to surface segregation suppression.

A series of growths were undertaken to investigate the influence of electron irradiation on enhancing dopant incorporation. Be was chosen as the target dopant for studying incorporation kinetics modification as (1) the potential for a ~100meV acceptor would be of significant technological importance for GaN and (2) serious problems are known to exist with surface segregation. Numerous Be-doped samples were investigated. It was found that electron irradiation significantly enhanced solubility for Be, decreasing surface segregation as indicated by the profile for a

step-doped layer as shown in Fig. 1, and suppressing inversion domain formation as indicated by the micrographs in Fig. 2. However, p-type material was never achieved, and photoluminescence studies indicated that the acceptor activation energy was more likely close to 200 meV. Thus, efforts with Be were discontinued.

Heavy Mg doping was investigated next. Although preliminary results indicated that electron irradiation could suppress surface segregation, detailed investigation of growth parameters also indicated that careful management of substrate temperature and Mg flux were as effective. Of interest, it was demonstrated that the p-carrier concentrations

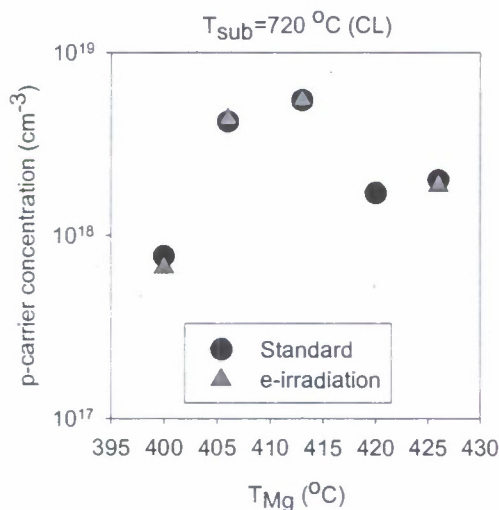


Figure 4. p-concentration for Mg doping as a function of Mg-oven temperature.

carrier concentration. What became clear after the numerous growths was that there was no statistical difference between growth with, and without, electron irradiation. Thus, the effects of electron irradiation are dominated by other surface chemistry effects, at least for the range of parameters investigated in this study.

Based on the obvious effects observed through photon irradiation observed by the other groups in this MURI, electron irradiation was investigated for altering In

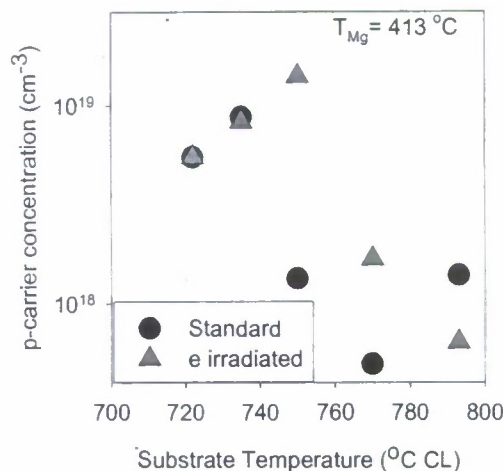


Figure 3. p-concentration for Mg doping as a function of substrate temperature.

could be achieved through careful temperature and flux management exceeded those typically reported for MBE, and explained the seemingly irreproducible reports of high p-concentration given for a small number of samples in the literature. The p-concentrations reported are approaching the levels needed for using GaN in HBT device structures, for example.

The increase in carrier concentration was accompanied by a decrease in mobility, but the overall conductivity increased with increasing

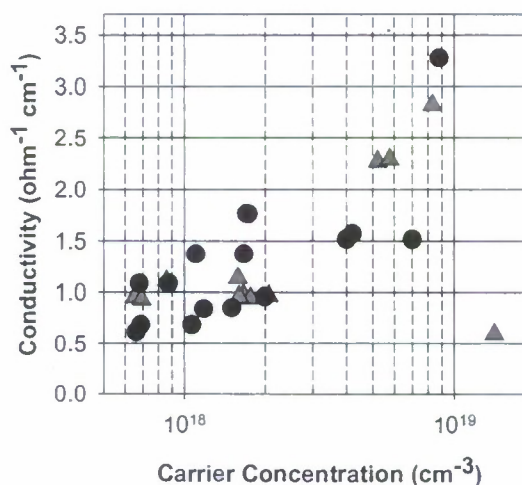


Figure 5. Comparison of conductivity for electron irradiated and standard growth of Mg-doped GaN.

Ts (oC)	PGa (10 <sup>-7</sup> Torr)	PIn (10 <sup>-8</sup> Torr)	x	x (e- irr.)
580	1.5	3.7	0	0
540	1.7	7.4	0	0
550	1.3	0.9	0.13	0.14
520	1.3	0.9	0.30	0.32
520	1.1	1.0	0.35	0.37
514	1.1	1.9	0.38	0.39
510	1.1	3.2	0.41	0.42
510	1.5	3.7	~0	~0

Table 1. Comparison of resulting x-values in electron irradiated and standard growth of InGaN for various substrate temperatures and growth flux ratios.

stoichiometry *in-situ*. In-situ control of stoichiometry is extremely difficult for the growth of various new classes of new materials. Such capability is crucial for development of epitaxial growth complex oxides, for example.  $\text{YMnO}_3$  was chosen as the vehicle for demonstration, and figure 6 illustrates some of the promising initial results. Further development of this technique into a quantitative tool is crucial for the next generation of epitaxial materials growth, and will be pursued under ONR funding..

#### Development of in-situ Cathodoluminescence

Cathodoluminescence (CL) was demonstrated to be a viable method of GaN substrate temperature determination during this funding period. This technique proved crucial for Mg doping study described above. The results have been published, and were presented as part of an invited talk at the Fall 2006 MRS meeting.

incorporation in InGaN growth. After growth of the sample set represented by the data summarized in Table 1, it was determined that electron irradiation, at least for the conditions investigated, did not result in a significant change in In incorporation. The primary effects were related to fraction of Ga overpressure and substrate temperature, suggesting the effects observed by others result primarily due to thermal effects.

WVU took the lead role for detailed discussions with the effort at Princeton to couple experimental and computational efforts, including having face-to-face meetings.

#### Development of in-situ RHEED-TRAX

RHEED-TRAX was demonstrated for its potential in detecting sub-monolayer coverage of material, and the ability to determine

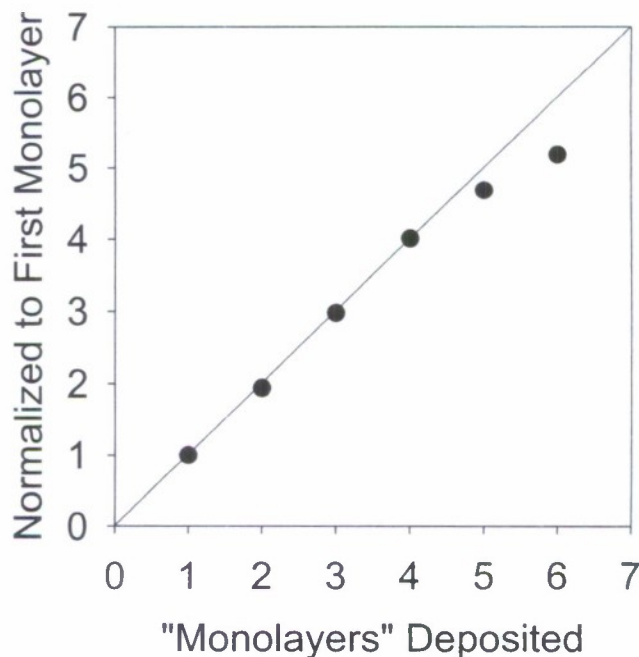


Figure 4. Linearity of RHEED-TRAX signal for Y monolayers deposited on GaN. The Y Ka signal was normalized to the Ga Ka signal.



## Final period planned efforts

### Modified Surface Energy Epitaxy (MOSEE) by E-beam excitation

- Investigate electron irradiation for demonstrate surface segregation suppression for heaviest Mg doping in GaN
- Demonstrate control of Mg surface segregation to control formation of selective polarity reversal

### Published papers

*"Thermal Activation of Beryllium-related Photoluminescence by Annealing of GaN Grown by Molecular Beam Epitaxy"*,

Kyoungnae Lee, B.L. VanMil, Ming Luo, Lijun Wang, N.C. Giles and T.H. Myers, *phys. stat. sol. (c)* 2(7), 2204-2207 (2005)

*"Oxygen adsorption and incorporation at irradiated GaN(0001) and GaN(0001)*

*surfaces: First-principles density-*

*functional calculations "*, Sun, Qiang, Selloni, A., Myers, T. H., Doolittle, W.A, *PHYSICAL REVIEW B* 74 (19): Art. No. 195317 NOV 2006 125

*"Compensation in Be-doped Gallium Nitride Grown Using Molecular Beam Epitaxy"*, K. Lee, B. VanMil, M. Luo, T. H. Myers, A. Armstrong, S. A. Ringel, M. Rummukainen and K. Saarinen, *GaN, AlN, InN and Related Materials. Symposium (Materials Research Society Symposium Proceedings Vol.892)*, 2006, p 729-34

*"The Use of Cathodoluminescence During Molecular Beam Epitaxy Growth of Gallium Nitride to Determine Substrate Temperature"*, K. Lee, E. D. Schires and T. H. Myers , *GaN, AlN, InN and Related Materials. Symposium (Materials Research Society Symposium Proceedings Vol.892)*, 2006, p 43-48

*"In-Situ Investigation of Surface Stoichiometry During InGaN and GaN Growth by Plasma-Assisted Molecular Beam Epitaxy Using RHEED-TRAXS"*, R.P. Tompkins, B. L. VanMil, E. D. Schires, K. Lee, Y. Chye, D. Lederman and T. H. Myers, *Mater. Res. Society Symp. Proceedings* 892, 55 (2006).

*"Molecular Beam Epitaxy of YMnO<sub>3</sub> on c-plane GaN"*, Y. Chye, T. Liu, D. Li, K. Lee, D. Lederman, and T. H. Myers, *Applied Physics Letters*, 88, 132906 (2006).

*"Energetics of Mg incorporation at GaN(0001) and GaN(000-1) surfaces"*, Qiang Sun, Annabella Selloni, T.H. Myers, A. Doolittle, *Phys. Rev. B.* 73 (15): 155337 APR 2006

*"Adsorption and diffusion of Ga and N adatoms on GaN surfaces: comparing the effects of Ga-coverage and electronic excitation"*, Noboru Takeuchi, Annabella Selloni, T.H. Myers, A. Doolittle, *Phys. Rev. B.* 72 (11): 115307 SEP 2005

*"The use of cathodoluminescence during molecular beam epitaxy growth of gallium nitride to determine substrate temperature"*, Kyoungnae Lee and T.H. Myers, *JOURNAL OF ELECTRONIC MATERIALS* 36 (4): 431-435 APR 2007

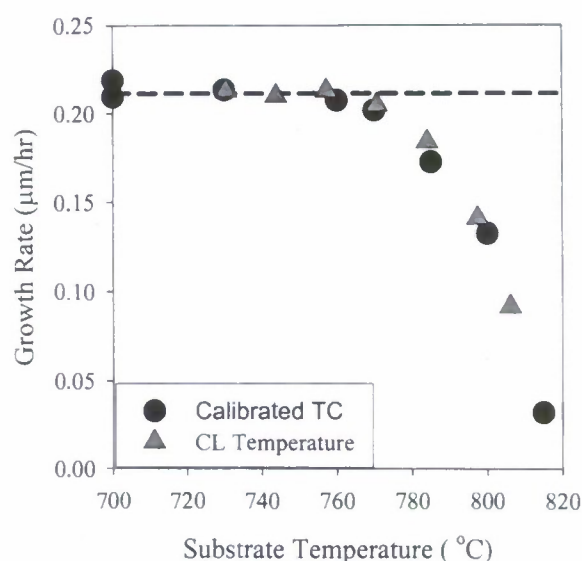


Figure 5. Comparison of the growth rate versus temperature with temperature determined by a carefully calibrated thermocouple and by CL

*"Polarization Electronics – A Path to Multifunctional Nanoscale Materials"*, Thomas H Myers and David Lederman, Proceedings of MELECON 2006. 2006 IEEE Mediterranean Electrotechnical Conference, 2006, p 3-10

*"Properties of YMnO<sub>3</sub> Self-assembled Nanocrystalline Prisms on GaN"*, Cameron Keenan, Sandeep Chandril, Esteban Ramos, A. L. Cabrera, Thomas H. Myers, and David Lederman, Accepted in Appl. Phys. Lett.

#### **Papers in Development:**

*"Be activation energy in GaN"* (to be submitted to APL)

*"Positron Annihilation Spectroscopy of Annealed and As-grown Be-doped GaN"* (to be submitted to APL – delayed by the untimely death of K. Saarinen)

*"RHEED-TRAX of YMnO<sub>3</sub> growth by molecular beam epitaxy"* (to be submitted to APL)

*"Direct measurement of Ga-overlayer formation during GaN growth by molecular beam epitaxy using RHEED-TRAX"* (to be submitted to APL)

#### **Students Supported**

##### **PhD (3)**

Cameron Keenan  
Kyoungnae Lee  
Sandeep Chandril

##### **Masters (0)**

##### **Undergraduate (0)**

## **Section 3) Princeton Contribution**

### **FIRST PRINCIPLES THEORETICAL MODELING OF ENERGETIC III-NITRIDE SURFACES**

**AFOSR GRANT F49620-03-1-0330**

Annabella Selloni, PI  
Department of Chemistry  
Princeton University

#### **1- Activity in 2007**

We started studying In adsorption and incorporation at the polar GaN surfaces, but incurred in difficulties that we attributed to the poor description of the electronic structure given by standard DFT calculations. This well known shortcoming of DFT is particularly evident when dealing



with In, e.g. InN is predicted to be metallic by DFT. As indicated by the experience of several groups, including ours, around the world, a possible way to overcome this difficulty is to use hybrid functionals (e.g. B3LYP), which include a fraction of exact Hartree Fock exchange in the DFT exchange correlation functional. However the efficient implementation of exact exchange within typical plane wave-pseudopotential codes is a quite challenging task. We have decided to carry out work in this direction and this has been our main activity in the last year. An article describing this work, entitled "Order N Implementation of Exact Exchange" (by Xifan Wu, Annabella Selloni, and Roberto Car), is in preparation. An abstract of this work is given below.

Exact (Hartree Fock) exchange is needed to overcome some of the limitations of local and semilocal approximations of density functional theory (DFT). Moreover exact exchange is a basic ingredient in modern approaches to compute excitation properties, like the GW and the OEP schemes. So far, however, computational cost has limited the use of exact exchange in plane wave calculations for extended systems. We show that this difficulty can be overcome by performing a unitary transformation from Bloch to Maximally Localized Wannier functions in combination with an efficient technique to compute real space Coulomb integrals. The resulting scheme scales linearly with system size and, when used in ab-initio molecular dynamics simulations, requires only a modest increase in computational cost compared to standard DFT implementations. We validate the scheme with representative applications.

## **2- Future activity: plans and goals**

We plan to apply the newly developed approach to understand the electronic structure of InGaN, mainly the character of the electron-hole states and their localization, and how these change with In concentration. The publications resulting from this work will appear after the end of this grant.

Final Note despite several requests, no annual report was received from Cornell, Bill Schaff.